

NICKEL COBALT BORON TERNARY ALLOYS

FIELD OF THE INVENTION

The present invention generally relates to ternary alloys containing nickel, cobalt, and boron that may be employed in place of chrome and chrome alloys
5 and methods of making the ternary alloys.

BACKGROUND OF THE INVENTION

Chromium is steel-gray, lustrous, hard, metallic, and takes a high polish. Chromium is a naturally occurring element present in the environment in several different forms. The most common forms are chromium (0), chromium (III), and
10 chromium (VI). The metal chromium, which is the chromium (0) form, is used for making steel. Chromium (VI) and chromium (III) are often used for chrome plating. Chromium (VI) is used as an anti-corrosion treatment and as an electrical shielding material for certain sheet metals. There are many desirable characteristics associated with chromium plating.

15 However, the use of chromium (VI) and its compounds are restricted in certain applications in some areas, primarily in the European Union. Broad legislative restrictions such as the Restriction of Hazardous Substances in the United States are expected to eliminate the use of chromium (VI) compounds in electronic products by 2006. Substitutes for chromium, especially in the plating
20 industry, are therefore desired.

SUMMARY OF THE INVENTION

The following presents a simplified summary of the invention in order to provide a basic understanding of some aspects of the invention. This summary
25 is not an extensive overview of the invention. It is intended to neither identify key or critical elements of the invention nor delineate the scope of the invention. Rather, the sole purpose of this summary is to present some concepts of the

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invention in a simplified form as a prelude to the more detailed description that is presented hereinafter.

5 The present invention provides nickel, cobalt, and boron ternary alloys that have a mirror bright deposit and a hardness on par with chrome. The desirable characteristics of the ternary alloys made in accordance with the present invention are, at least in part, attributable to the use of certain brighteners in the electroplating bath. The brighteners facilitate deposition of metal ions on the cathode in such a manner as to result in electroplated nickel cobalt boron ternary alloys having numerous desirable properties. For example, 10 the brighteners facilitate deposition of metal ions at relatively low current densities, thereby increasing the bright plating range. Consequently, the nickel cobalt boron ternary alloys may take the place of electroplated chrome and chromium alloys, thereby providing potential environmental benefits.

15 One aspect of the invention relates to methods of electroplating an alloy containing nickel cobalt boron involving providing an electroplating bath containing an anode, a cathode, water, ionic nickel, ionic cobalt, ionic boron, and at least one brightener selected from the group consisting of sulfur containing brighteners and organic brighteners; and applying a current so that a nickel cobalt boron alloy forms on/at the cathode.

20 To the accomplishment of the foregoing and related ends, the invention comprises the features hereinafter fully described and particularly pointed out in the claims. The following description and the annexed drawings set forth in detail certain illustrative aspects and implementations of the invention. These are indicative, however, of but a few of the various ways in which the principles 25 of the invention may be employed. Other objects, advantages and novel features of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the drawings.

BRIEF SUMMARY OF THE DRAWINGS

Figure 1 illustrates a schematic diagram of a nickel cobalt boron alloy electroplating system in accordance with one aspect of the present invention.

5 Figure 2 is a graph showing the type of metal deposit at specific current densities for a conventional electroplating bath.

Figure 3 is a graph showing the type of metal deposit at specific current densities for other conventional electroplating baths.

Figure 4 is a graph showing the type of metal deposit at specific current densities for electroplating baths used in accordance with the present invention.

10 DETAILED DESCRIPTION OF THE INVENTION

The present invention provides ternary alloys made by electroplating that exhibit two or more of high brightness, high luster, level/smooth, uniform thickness, high hardness, high reflectivity, ductile, high density, resistant to corrosion, resistant to heat, and resistant to wear. Typically, the ternary alloys made in accordance with the present invention have a mirror bright deposit and a hardness on par with chrome. Electroplating involves metal in ionic form migrating in solution from a positive electrode (anode) to a negative electrode (cathode). The anode and cathode are connected to a power source and an electrical current is passed through the electroplating bath or solution causing substrates at the cathode to be coated by the metal (nickel, cobalt, and alloy metal) in solution. In most embodiments, the substrate to be plated is the cathode.

25 The cathodes are any electrically conductive material that can accommodate a nickel cobalt ternary alloy plating while resisting degradation by the acidic nature of the catholyte. The cathode substrates include metal structures and non-metal structures. Metal structures, or structures with a metal surface contain surfaces of one or more of aluminum, bismuth, cadmium, chromium, copper, brass, gallium, germanium, gold, indium, iridium, iron, lead,

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magnesium, nickel, palladium, platinum, silver, steel, stainless steel, tin, titanium, tungsten, zinc, alloys thereof, and the like. Non-metal structures include plastics, circuit board prepregs (including materials such as glass, epoxy resins, polyimide resins, Kevlar®, Nylon®, Teflon®, etc.), ceramics, metal oxides, and the like.

5 The electroplating bath is typically an aqueous solution. In addition to water, the electroplating bath (or the catholyte and anolyte if a separator is employed) may optionally contain one or more co-solvents. Such co-solvents include water-miscible solvents such as alcohols, glycols, alkoxy alkanols, ketones, and various other aprotic solvents. Specific examples of co-solvents
10 include methanol, ethanol, propanol, ethylene glycol, 2-ethoxy ethanol, acetone, dimethyl formamide, dimethyl sulfoxide, acetonitrile, and the like.

Prior to placing the substrate/cathode in the electroplating bath, it may be optionally pretreated, washed and/or activated. Pretreatment may include cleaning with alcohol and/or with an anionic solution. Washing may include an
15 anodically cleaning in an alkaline solution in the presence of a negative current, rinsing in hot or cold distilled or deionized water, and/or immersing in an acid bath. Activation includes one or both of anodically activating by passing a negative current through an acidic activator bath and cathodically activating by passing a positive current through an acidic activator bath. An advantage of the
20 cleaning process is that the substrate is free of contaminant, such as oxides when placed in the plating bath eliminating the possible need for sequestering agents to prevent precipitation or the formation of sludge in the electroplating bath.

In the electroplating bath, platable nickel and cobalt are present in ionic
25 form, and platable boron is present in ionic form or in an ionic complex. Although platable boron may be present in ionic form or in an ionic complex, it is henceforth referred to as ionic boron for brevity. Sources of ionic nickel, cobalt, and boron are typically the corresponding nickel, cobalt, and boron salts and optionally an anode that contains one or more of nickel, cobalt, and boron.

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Boron may alternatively be introduced into the electroplating bath by a boron containing acid, an amino-borane compound, and/or an amine-borane compound (collectively referred to as boron containing compounds). The boron containing acid does not include boric acid, as boric acid improves conductivity and/or is used as a pH adjuster. It is noted that the boric acid does not provide a significant portion of platable boron, although in some instances it may provide minor amounts of platable boron.

Examples of nickel, cobalt, and boron salts and boron containing compounds include nickel acetate, nickel acetylacetonate, nickel ethylhexanoate, nickel carbonate, nickel formate, nickel nitrate, nickel oxalate, nickel sulfate, nickel sulfamate, nickel sulfide, nickel chloride, nickel fluoride, nickel iodide, nickel bromide, nickel oxide, nickel tetrafluoroborate, nickel phosphide, cobalt acetate, cobalt acetylacetonate, cobalt ethylhexanoate, cobalt carbonate, cobalt nitrate, cobalt oxalate, cobalt sulfate, cobalt chloride, cobalt fluoride, cobalt hydroxide, cobalt iodide, cobalt bromide, cobalt oxide, cobalt boride, cobalt tetrafluoroborate, boron nitride, boron trichloride, boron trifluoride, boron triiodide, boron tribromide, boron oxide, boron phosphate, dimethylamine borane, morpholine borane, dimethylamino borane, dimethylsulfide borane, t-butylamine borane, ammonia borane, N,N-diethylaniline borane, diphenylphosphine borane, dimethylaminopyridine borane, ethylmorpholine borane, methylmorpholine borane, 2,6-lutidine borane, morpholine borane, oxathiane borane, phenylmorpholine borane, pyridine borane, tetrahydrofuran borane, tributylphosphine borane, triethylamine borane, trimethylamine borane, borax, and hydrates thereof.

The anodes are electrically conductive materials, and optionally contain materials that can deliver one or more of nickel, cobalt, and boron ions into the electroplating solution. Accordingly, in one embodiment, the anode contains at least one or more of nickel, cobalt, and boron, and optionally other materials. In this embodiment, the anode is a working anode. There is an economic

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5 advantage associated with generation of ternary metal alloy ions from the working anodes. In particular, compared to providing metal ions from a liquid concentrate (such as a nickel salt), the cost of one or more of nickel, cobalt, and boron via an anode is a fraction of that from the liquid concentrate (such as about one-quarter of the cost or less including about one-eighth of the cost). Solid working anodes are also advantageous in that they are markedly easier to handle, store, and transport, compared with liquid concentrates of one or more of nickel, cobalt, and boron salts. In another embodiment, the anode is an inert anode containing materials such as iridium oxide, platinum, titanium, platinum-titanium, graphite, carbon, and the like.

10 The electroplating bath contains an amount of ionic nickel, cobalt, and boron to facilitate electroplating the ternary alloy, typically, on the cathode. In one embodiment, the electroplating bath contains about 10 g/l or more and about 150 g/l or less of ionic nickel, about 0.5 g/l or more and about 70 g/l or less of ionic cobalt, and about 0.1 g/l or more and about 20 g/l or less of ionic boron. In another embodiment, the electroplating bath contains about 40 g/l or more and about 100 g/l or less of ionic nickel, about 1 g/l or more and about 30 g/l or less of ionic cobalt, and about 0.2 g/l or more and about 10 g/l or less of ionic boron. In yet another embodiment, the electroplating bath contains about 50 g/l or more and about 70 g/l or less of ionic nickel, about 3 g/l or more and about 6 g/l or less of ionic cobalt, and about 0.3 g/l or more and about 6 g/l or less of ionic boron.

20 In some instances, the ratio of boron to cobalt and/or the ratio of either boron or cobalt to nickel in solution is set to facilitate an orderly and high quality deposition of the ternary alloy on the substrate. For instance, in one embodiment, the ratio of boron to cobalt is from about 1:4 to about 3:1 while the ratio of at least one of boron and cobalt to nickel is from about 1:20 to about 1:5. In another embodiment, the ratio of boron to cobalt is from about 1:3 to about 2:1 while the ratio of at least one of boron and cobalt to nickel is from about 1:15 to about 1:10.

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In order to obtain a nickel cobalt boron ternary alloy with desirable properties, it is necessary to employ at least one brightener. Two or more brighteners can be used. Although not wishing to be bound by any theory, it is believed that the active deposition of nickel, cobalt, and boron metal species simultaneously is complex, due to differences in characteristics between these metals, and that the presence of at least one brightener as described herein facilitates the orderly plating of the metals on a substrate such that beneficial properties are realized when compared to a nickel cobalt boron ternary alloy made without one or more brighteners as described herein.

The brighteners that may be employed in the nickel cobalt boron electroplating bath include sulfur containing brighteners and organic brighteners. In one embodiment, the electroplating baths contain from about 0.001% to about 5% by weight of at least one brightener. In another embodiment, the electroplating baths contain from about 0.005% to about 2.5% by weight of at least one brightener. In yet another embodiment, the electroplating baths contain from about 0.01% to about 1% by weight of at least one brightener.

In one embodiment, the ternary alloy electroplating baths contain an effective amount of at least one sulfur containing brightener to improve the quality of the alloy deposit. Improvements in the alloy deposit include improving such characteristics such as one or more of the brightness of the deposited alloy, the luster of the deposited alloy, the levelness of the deposited alloy, the hardness of the deposited alloy, the reflectivity of the deposited alloy, and the similarity in appearance to a high quality chromium deposit. General examples of sulfur containing brighteners include sulfinic acids, sulfonic acids, aromatic sulfonates, aromatic sulfinates, sulfonamides, sulfonimides, sulfimides, sulfo-betaines, and the water-soluble salts of these materials. Examples sulfur containing brighteners include the alkyl naphthalene and benzene sulfonic acids, the benzene and naphthalene di- and trisulfonic acids, benzene and naphthalene sulfonamides, and sulfonimides such as saccharin, vinyl and allyl sulfonamides

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and sulfonic acids.

Specific examples of sulfur containing brighteners include sodium saccharinate; trisodium 1,3,6-naphthalene trisulfonic acid; trisodium 1,3,7-naphthalene trisulfonic acid; benzene sulfinic acid; sodium styrene sulfonate; p-toluene sulfinic acid; p-toluene sulfonic acid; propyl sulfonic acid; beta-hydroxy propyl sulfonic acid; ditolylsulfimide; sodium salt of di-o-tolyl disulfimide; sodium salt of dibenzene disulfimide; pyridine-3-sulfonic acid; p-vinylbenzene sulfonic acid; sodium allyl sulfonate; sodium vinyl sulfonate; sodium propargyl sulfonate; sodium o-sulfobenzimide; disodium 1,5-naphthalene disulfonate; sodium benzene monosulfonate; dibenzene sulfonimide; sodium benzene monosulfinate; sodium allyl sulfonate; sodium 3-chloro-2-butene-1-sulfonate; monoallyl sulfamide; diallyl sulfamide; 1(gamma-sulfopropoxy)-2-butyne-4-ol; 1,4-di(beta-hydroxy-gamma-sulfonic propoxy)-2-butyne; allyl sulfonamide; quinaldyl-N-propanesulfonic acid betaine; quinaldine dimethyl sulfate; isoquinaldyl-N-propanesulfonic acid betaine; isoquinaldine dimethyl sulfate; disulfonated 1,4-di(beta-hydroxyethoxy)-2-butyne; and sulfonated 1-(beta-hydroxyethoxy)-2-propyne. Many sulfur containing brighteners are described in U.S. Patent 3,922,209; 4,036,709; 4,053,373; and 4,421,611 which are hereby incorporated by reference.

Sulfo-betaines are heterocyclic compounds having Formula I:

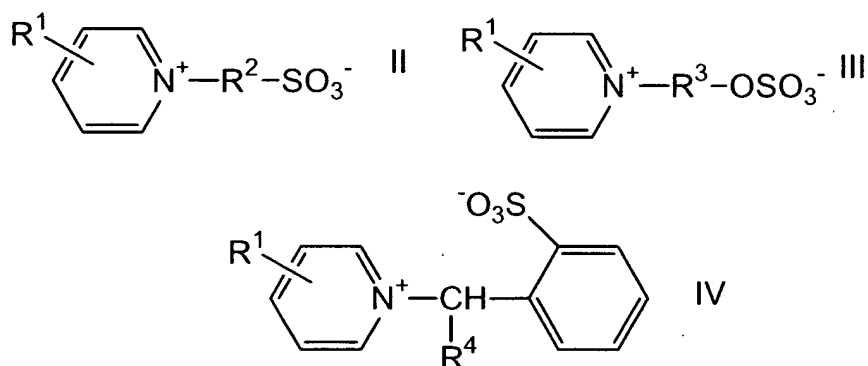


wherein RN is an aromatic heterocyclic nitrogen-containing group, and R' is an alkylene or hydroxy alkylene group. Generally, the RN group is an aromatic nitrogen-containing group such as pyridine, substituted pyridines, quinoline, substituted quinolines, isoquinoline, substituted isoquinolines, benzimidazoles, and acridines. Various substituents can be incorporated into the aromatic nitrogen-containing groups specified above, and the substituent may be attached

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to the various positions of the aromatic group. Examples of substituents include hydroxy, alkoxy, halide, lower alkyl, lower alkenyl, amino alkyl, mercapto, cyano, hydroxyalkyl, acetyl, benzoyl, etc.

The sulfo-betaine compounds can also be characterized by Formulae II, III, and IV:



wherein R¹ is hydrogen, benzo(b), or one or more lower alkyl, halide, hydroxy, lower alkenyl or lower alkoxy groups; R² is an alkylene or hydroxy alkylene group containing three or four carbon atoms in a straight chain; R³ is an alkylene or hydroxy alkylene group containing two or three carbon atoms in a straight chain; and R⁴ is a hydrogen or a hydroxyl group.

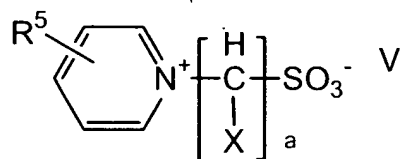
As indicated in Formulae II, III, and IV, the sulfobetaines contain a pyridinium portion which may be an unsubstituted pyridine ring or a substituted pyridine ring. Thus, R¹ may be one or more lower alkyl groups, halogen groups, lower alkoxy groups, hydroxy groups or lower alkenyl groups.

Examples of the pyridine groups which may be included in the above Formulae II-IV include pyridine, 4-methyl pyridine (picoline), 4-ethyl pyridine, 4-t-butyl pyridine, 4-vinyl pyridine, 3-chloro pyridine, 4-chloro pyridine, 2,3 or 2,4 or 2,6 or 3,5-di-methyl pyridine, 2-methyl-5-ethyl pyridine, 3-methyl pyridine, 3-hydroxy pyridine, 2-methoxy pyridine, and 2-vinyl pyridine.

In Formula II, R² can be an alkylene or hydroxy alkylene group containing three or four carbon atoms in a straight chain which may contain alkyl

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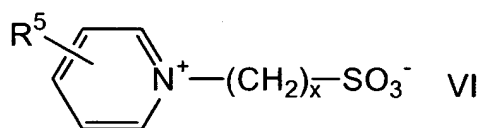
substituents which may be represented by Formula V



wherein R⁵ is hydrogen or a lower alkyl group, one X is hydrogen, hydroxy or a hydroxy methyl group, the remaining X is hydrogen and a is 3 or 4.

5 The preparation of the sulfo-betaines of Formula II wherein R² is an alkylene radical is described in, for example, U.S. Patent 2,876,177, which is hereby incorporated by reference. Briefly, the compounds are formed by reaction of pyridine or a substituted pyridine with lower 1,3- or 1,4-alkyl sultones. Examples of such sultones include propane sultone and 1,3- or 1,4-butane
10 ammonium-N-propane-omega-sulfonic acids or the corresponding butane derivative, depending on the alkyl sultone used.

Examples of sulfo-betaines of Formula II wherein R² is an alkylene group may be represented by Formula VI:

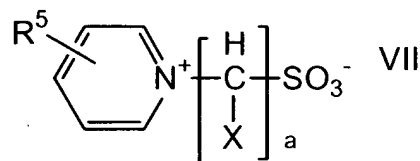


15 wherein R⁵ is hydrogen, one or more lower alkyl groups or a benzo(b) group, and x is 3 or 4.

The preparation of the sulfo-betaine of Formula II wherein R² is a hydroxy alkylene group is described in, for example, U.S. Patent 3,280,130, which is hereby incorporated by reference. The method involves a first reaction step wherein pyridine is reacted with epichlorohydrin in the presence of hydrochloric
20 acid, and, thereafter, in a second reaction step, the quaternary salt formed thereby is reacted with sodium sulfite.

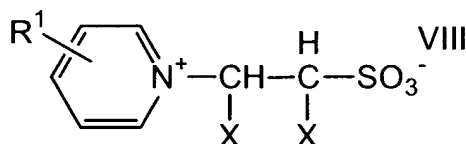
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Examples of the sulfo-betaines wherein R² is a hydroxy alkylene group including pyridine compounds of the Formula VII:



wherein R⁵ is hydrogen, one or more lower alkyl groups or a benzo(b) group, a is 3 or 4, one X substituent is a hydroxyl group and the other are hydrogen. In an alternative embodiment, two of the X groups could be hydrogen and the third X group can be a hydroxy alkyl group, such as a hydroxy methyl group.

The sulfo-betaines include the type represented by Formula III above wherein R¹ is defined as in Formula I, and R³ is an alkylene or hydroxy alkylene group containing two or three carbon atoms in a straight chain and optionally pendant hydroxyl groups, hydroxyl alkyl groups or alkyl groups containing one or two carbon atoms. Examples of the betaines represented by Formula III are those wherein R¹ includes pyridine compounds of Formula VIII:



wherein R¹ is hydrogen, a lower alkyl group or a benzo(b) group, and both X groups are hydrogen or one X is hydrogen and the other is a hydroxyl group.

The preparation of the sulfo-betaines of the type represented by Formulae III and VIII which are known as pyridinium-alkane sulfate betaines is known in the art. For example, the sulfate betaines can be prepared by reacting a pyridine compound with an alkanol compound containing a halogen atom to form an intermediate hydroxylalkyl pyridinium-halide which is thereafter reacted with the corresponding halosulfonic acid to form the desired betaine. Specifically, pyridinium-(ethyl sulfate-2) betaine can be prepared by reacting ethylene

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chlorohydrin with pyridine followed by reaction with chlorosulfonic acid. The details of the procedure are described in U.S. Patent 3,314,868 which is hereby incorporated by reference. Other alkanol compounds containing a halogen which can be reacted with pyridine to form the desired betaines include

5 1-chloro-2-propanol, 3-chloro-1-propanol, etc.

Betaines also include those represented by Formula IV given above which may be obtained by reacting, for example, o-chloro benzyl chloride (prepared from o-chloro benzaldehyde) with pyridine or a substituted pyridine followed by replacement of the o-chloro group with a sulfonic acid group. Although a similar

10 reaction can be conducted with the corresponding meta and para chloro compounds, the ortho derivative tend to perform better in the electroplating baths of the present invention.

In another embodiment, the ternary alloy electroplating baths contain an effective amount of at least one organic brightener to improve the quality of the alloy deposit. General examples of organic brighteners include acetylenic

15 alcohols, ethylenic alcohols, acetylenic amines, acetylenic esters, acetylenic sulfonic acids and sulfonates, alkoxylated acetylenic alcohols such as ethoxylated and propoxylated acetylenic alcohols, acetylenic carboxylic acids such as 3-(2-propynoxy)-2-propenoic acid, coumarins, aldehydes, compounds

20 containing the $C\equiv N$ linkage, and N-heterocyclics.

Specific examples of organic brighteners include ethoxylated butynediol; 2-butyne-1,4-diol; propargyl alcohol; thiodipropionitrile; ethoxylated propargyl alcohol; hydroxyethyl propynyl ether; beta-hydroxypropyl, propynyl ether; gamma-propynoxy, gamma-propynoxy, bis-beta-hydroxyethyl ether

25 2-butyne-1,4-diol; bis-beta-hydroxypropyl ether 2-butyne-1,4-diol; 1,4-di-(beta-hydroxyethoxy)-2-butyne; 1,4-di-(beta-hydroxy-gamma-chloropropoxy)-2-butyne; 1,4-di-(beta-gamma-epoxypropoxy)-2-butyne; 1,4-di-(beta-hydroxy-gamma-butenoxy)-2-butyne; 1,4-di-(2'-hydroxy-4'-oxa-6'-heptenoxo)-2-butyne;

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N-(2,3-dichloro-2-propenyl)-pyridinium chloride; 2,4,6-trimethyl N-propargyl pyridinium bromide; N-allylquinaldinium bromide; 2-methyl-3-butyn-2-ol; N-allylpyridinium bromide; N-allylisoquinaldine bromide;

1-(beta-hydroxyethoxy)-2-propyne; 1-(beta-hydroxypropoxy)-2-propyne; phenosafranin; and fuchsin. Many acetylenic derivatives that may be employed as organic brighteners in the ternary alloy electroplating baths include those described in the U.S. Patents 3,133,006; 3,140,988; 3,152,975; 3,160,574; 3,170,853; 3,305,462; 3,366,557; 3,699,016; 3,378,470; 3,502,550; 3,515,652; 3,711,384; 3,719,568; 3,723,260; 3,759,803; 3,795,592; 3,860,638; 3,862,019; 3,844,773; 3,898,138; 3,907,876; 3,969,198; 4,036,709; 4,054,495; 4,062,738; and 4,421,611, which are hereby incorporated by reference.

The electroplating baths may optionally contain one or more of a number of additives. Such additives include complexing agents, chelating agents, surfactants, wetting agents, hardening agents, pH adjusters, leveling agents, reducing agents, antipitting agents, promoters, antioxidants, stress relief agents, conductivity salts, and the like. In one embodiment, the electroplating baths contain from about 0.001% to about 5% by weight of each of the additives.

In embodiments where the ternary alloy contains iron, the electroplating bath optionally contains one or more bath-soluble complexing agents for iron. Such complexing agents may be amine-containing complexing agents or aliphatic carboxylic acids containing from about 1 to about 3 carboxyl groups and from about 1 to about 6 hydroxyl groups. The carboxyl group may be present as -COOH, as the anion -COO⁻ in solution, or in the form of an internal lactone such as present in the sugars. Examples of complexing agents in the hydroxy substituted lower aliphatic carboxylic acids having from about two to about eight carbon atoms include ascorbic acid, isoascorbic acid, citric acid, malic acid, glutaric acid, gluconic acid, muconic acid, glutamic acid, glycollic acid, aspartic acid, dextrose, sucrose, and the like. Examples of amine-containing complexing agents include nitrilotriacetic acid and ethylene diamine tetra-acetic acid.

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Alternative complexing agents include water soluble salts of ammonium, alkali metal, and iron salts.

5 The complexing agents facilitate keeping the metal ions, particularly the ferrous and ferric ions, in solution thereby preventing precipitation of iron as ferric hydroxide. In one embodiment, the electroplating bath contains from about 5 to about 100 grams/liter of the complexing agent to provide a mole ratio of complexing agent to iron ions in the bath of from about 1:1 to about 50:1.

10 The optional incorporation of wetting or surface active agents (surfactants) and particularly anionic wetting agents into the electroplating baths of the invention sometimes results in a ternary alloy plating with improved leveling and brightness, and/or the electroplating baths exhibit improved stability compared to an electroplating bath without wetting or surface active agents. The incorporation of surfactants may in some instances mitigate gas streaking and pitting.

15 Wetting agents promote leveling and brightening, as well as promoting bath stability. Examples of wetting agent include polyoxyalkylated naphthols; ethylene oxide/polyglycol compounds; sulfonated wetting agents; carbowax type wetting agents; and the like.

20 Surfactants contribute to the overall stability of the bath and improve various properties in the resultant tin alloy layer. General examples of surfactants include one or more of a nonionic surfactant, cationic surfactant, anionic surfactant, and amphoteric surfactant. Specific examples of surfactants include nonionic polyoxyethylene surfactants; alkoxylated amine surfactants; ethylene oxide-fatty acid condensation products; polyalkoxylated glycols and
25 phenols; betaines and sulfobetaines; amine ethoxylate surfactants; quaternary ammonium salts; pyridinium salts; imidazolinium salts; sulfated alkyl alcohols; sulfated lower ethoxylated alkyl alcohols; sodium lauryl sulfonate; sodium sulfate derivative of 2-ethyl-1-hexanol and sodium dialkyl sulfosuccinates such as the dihexyl ester of sodium sulfosuccinic acid; and the like.

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5 The optional incorporation of leveling agents in some instances promotes the formation of a smooth surface of the electroplated tin alloy layer, even if the cathode surface on which the tin alloy layer is formed is not smooth. Examples of leveling agents include the condensation products of thiourea and aliphatic aldehydes; thiazolidinethiones; imidazolidinethiones; quaternized polyamines; and the like. Specific examples of leveling agents include 1-(sulfopropyl)pyridinium hydroxide and (1-sulfo-2-hydroxypropyl)pyridinium hydroxide.

10 Suitable hardening agents include 2-butyne-1,4-diol, phenylpropionic acid, 2-butyne-1,4-disulfonic acid, 3-dimethylamino-1-propyne and bis(trimethylamine)-1,2-diphenyl-1,2-bis(dichloroboryl)ethylene. The hardener effectively makes grain size more fine and slows down the rate at which the nickel, boron, and cobalt ions reach the substrate. This thereby provides a more uniform deposition of the coating on the substrate.

15 The optional incorporation of one or more conductivity salts in some instances enhances the conductivity of the electroplating solution, such as by varying the chloride content or by the addition of conductivity salts. In one embodiment, such conductivity salts are added during make up of the electroplating bath. Examples of conductivity salts include boric acid, sodium sulfate, sodium chloride, potassium sulfate, potassium chloride, and the like.
20 Higher conductivity generally means that lower operating electrical costs are realized. It also may allow the application of more current from rectifiers with lower voltage maximums. Finally, higher conductivity may allow for improved current carrying capacity into confined plating spaces. In one embodiment, the electroplating bath contains from about 5 g/L to about 200 g/L of a conductivity salt.
25 In another embodiment, the electroplating bath contains from about 10 g/L to about 150 g/L of a conductivity salt.

 In one embodiment, a catalyst is not included in the electroplating bath. In another embodiment, a chromium compound is not included in the

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electroplating bath. In yet another embodiment, a cyanide compound is not included in the electroplating bath. In still yet another embodiment, a lead compound is not included in the electroplating bath. In these embodiments, the electroplating bath is environmentally friendly.

5 The pH of the electroplating bath is maintained to promote the efficient plating of the ternary alloy on the substrate/cathode. In one embodiment, the pH of the electroplating bath is about 2 or more and about 6 or less. In another embodiment, the pH of the electroplating bath is about 3 or more and about 5 or less. In yet another embodiment, the pH of the electroplating bath is about 3.5
10 or more and about 4.5 or less. The pH of the electroplating bath may be adjusted using additions of the acid or a base compound. The acids are relatively strong acids that are not oxidizing acids. Examples of acids include sulfuric acid, trifluoroacetic acid, phosphoric acid, polyphosphoric acid, fluoboric acid, hydrochloric acid, acetic acid, alkane sulfonic acids, and alkanol sulfonic
15 acids. Bases include hydroxide compounds, such as ammonium hydroxide, tetraalkylammonium hydroxide, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, lithium carbonate, nickel carbonate, cobalt carbonate, lithium bicarbonate, nickel bicarbonate, cobalt bicarbonate, and the like.

20 The temperature of the electroplating bath is maintained to promote the efficient plating of the ternary alloy on the substrate/cathode. In one embodiment, the temperature of the electroplating bath, during plating, is about 10° C. or more and about 90° C. or less. In another embodiment, the temperature of the electroplating bath is about 30° C. or more and about 80° C.
25 or less. In yet another embodiment, the temperature of the electroplating bath is about 40° C. or more and about 70° C. or less.

Any suitable source of power is connected to the electrodes, such as direct current, alternating current, pulsed current, periodic reverse current, or combinations thereof. A current density is imposed from an energy source

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through the electrodes causing nickel, cobalt, and boron ions from the electroplating bath to migrate towards and attach to the substrate/cathode forming a layer of a nickel, cobalt, and boron alloy thereon. In one embodiment, current densities of about 1 ASF or more and about 500 ASF or less are employed. In another embodiment, current densities of about 5 ASF or more and about 200 ASF or less are employed. In yet another embodiment, current densities of about 10 ASF or more and about 100 ASF or less are employed. In still yet another embodiment, current densities of about 2 ASF or more and about 40 ASF or less are employed. In still yet another embodiment, current densities of about 4 ASF or more and about 35 ASF or less are employed.

Circulation of the bath in the tank is optionally provided by any suitable means, such as a filtration system and/or air agitation system. Circulation and agitation facilitates keeping the anodes active, and provides benefits to the ternary alloy forming reaction by keeping ion concentrations substantially equal in all areas of the electroplating bath, and in some instances contributes to the resultant brilliant appearance of the alloys. For example, a pump may continuously or intermittently, as needed, pump the electroplating bath through a filter to provide the circulation and to remove contaminants and any other particles which may undesirably precipitate out of the electroplating bath. An air agitation system also may operate to circulate the solution in the electroplating bath. The components of the electroplating bath may be replenished as necessary to facilitate the electroplating process.

The length of time that the substrate/cathode is in contact with the electroplating bath under a specified current density depends upon the desired thickness of the resultant ternary alloy layer and the concentrations of the electroplating bath components. In one embodiment, the substrate/cathode is in contact with the electroplating bath (period of time from the when the nickel, cobalt, and boron alloy begins to form until the ternary alloy is removed from the bath) under a specified current density for a time of about 1 second or longer

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and about 120 minutes or shorter. In another embodiment, the substrate/cathode is in contact with the electroplating bath (under plating conditions) under a specified current density for a time of about 5 seconds or longer and about 60 minutes or shorter. In yet another embodiment, the substrate/cathode is in contact with the electroplating bath (under plating conditions) under a specified current density for a time of about 10 seconds or longer and about 30 minutes or shorter.

The ternary alloy electroplating bath optionally contains at least one selective membrane, such as ionic and nonionic selective membranes, positioned between the anode and cathode. The membranes may function as diffusion barriers. The presence of a selective membrane forms a catholyte around the cathode and an anolyte around the anode, where the catholyte is typically the electroplating bath. Selective membranes may have one or more of the following properties: permit the passage therethrough of certain ionic species while preventing the passage therethrough of other ionic species; permit the passage therethrough of nonionic species while preventing the passage therethrough of ionic species; prevent or mitigate the migration of additives of the catholyte to the anode; and/or prevent substantial amounts of metal cations from migrating from the catholyte to the anolyte. For example, the selective membrane may permit the flow of water therethrough, for instance osmotically, while preventing the passage of metal ions therethrough. In some instances, the migration of additives of the catholyte to the anode may produce undesirable species at the anode.

The electroplating bath, and valves that permit components to enter the electroplating bath may be equipped with flow meters and/or flow controllers to measure and control the amount of components entering into the electroplating bath. The flow meter and/or a flow controller may be connected to a computer/processor including a memory to facilitate measuring and controlling the amount of individual components that flow into the electroplating bath and/or

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for automated process control of the ternary alloy electroplating method. The computer/processor may be further coupled to sensors in the electroplating bath to measure one or more of pH, species concentration, volume, and the like. The computer/processor may be coupled to control valves that permit introduction of additional water, metals, anode replacement, acid, and/or base, into the electroplating bath.

Referring to Figure 1, an exemplary arrangement of a method and nickel cobalt boron alloy plating system are described. The ternary alloy plating system 100 includes a power source (not shown) for providing current to an electrochemical cell 102 containing an aqueous electroplating bath. The electrochemical cell 102 may contain an optional selective membrane 106, which subdivides the bath into a catholyte or electroplating bath 108 and an anolyte 110 (and this general arrangement may be repeated one or more times in an adjacent fashion to provide multiple electrochemical cells with a plurality of anolytes 110, catholytes 108, and selective membranes 106). The ternary alloy plating system 100 also contains an anode 112 and a cathode 114. The catholyte or electroplating bath 108 contains the ionic metals as described above while the anolyte 110 contains any acidic, basic, or neutral solution that can carry a current. Current is run through the electrochemical cell 102 inducing the deposition or plating of a nickel cobalt boron alloy at the cathode 110. If the optional selective membrane 106 is not present, which occurs in a more traditional set-up, there is no separate anolyte and catholyte, but only an electroplating bath in the electrochemical cell 102.

Optionally, after the ternary alloy is formed, the ternary alloy may be heat treated to improve its hardness. For example, the nickel cobalt boron ternary alloy may be heated from about 200 °C. to about 700 °C., and more specifically from about 250 °C. to about 550 °C., for a sufficient period of time to improve hardness.

The ternary alloy formed in accordance with the present invention mainly

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contains nickel, cobalt, and boron. In one embodiment, the ternary alloy contains from about 30 % to about 80 % by weight of nickel, from about 30 % to about 80 % by weight of cobalt, and from about 0.01 % to about 10 % by weight of boron. In another embodiment, the ternary alloy contains from about 40 % to about 70 % by weight of nickel, from about 40 % to about 70 % by weight of cobalt, and from about 0.1 % to about 5 % by weight of boron.

While the ternary alloy formed in accordance with the present invention mainly contains nickel, cobalt, and boron, other components may be present including minor amounts (such as less than about 2 % by weight) of other compounds. For example, the ternary alloy may contain minor amounts of one or more of the additives to the bath, contaminants, or another metal. In another embodiment, the ternary alloy formed in accordance with the present invention contains less than about 1 % by weight of other components (not nickel, cobalt, or boron). In yet another embodiment, the ternary alloy formed in accordance with the present invention contains less than about 0.1 % by weight of other components.

The nickel, cobalt, and boron ternary alloy formed in accordance with the present invention, can have a thickness as small as about 0.5 μm with substantially no pores. In another embodiment, the thickness of the ternary alloy formed in accordance with the present invention can be as small as about 1 μm with substantially no pores.

The nickel, cobalt, and boron ternary alloys formed in accordance with the present invention may have high hardness values, when measured using a Vickers hardness measuring device having 100 gm loads. In one embodiment, the hardness of the ternary alloy formed in accordance with the present invention is at least about 600 as deposited, and at least about 900 after optional heat treatment. In another embodiment, the hardness of the ternary alloy formed in accordance with the present invention is at least about 1,000 as deposited, and at least about 1300 after optional heat treatment. In yet another embodiment,

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the hardness of the ternary alloy formed in accordance with the present invention is at least about 1,050 as deposited, and at least about 1400 after optional heat treatment.

5 The resultant nickel cobalt boron alloy layer electroplated in accordance with the present invention has many desirable characteristics including one or more of high brightness, high hardness, excellent lubricity, corrosion resistance, uniform thickness, excellent leveling, excellent ductility, lack of pinholes, environmentally friendly processing, and controllable thickness.

10 Uniform thickness means uniform in two senses. First, a uniformly thick ternary alloy layer results when electroplating a smooth or curvilinear surface cathode and the nickel cobalt boron alloy layer has substantially the same thickness in any location after removal from the surface of the cathode. This uniformly thick ternary alloy layer is smooth and flat when the surface of the cathode is smooth while the uniformly thick ternary alloy layer may have an
15 uneven surface mimicking the uneven contours of the underlying cathode surface. Second, a uniformly thick ternary alloy layer results when electroplating an uneven cathode surface so that the resultant nickel cobalt boron alloy layer appears smooth and the ternary alloy layer has substantially the same thickness within locally smooth regions on the surface of the cathode. This second sense
20 also refers to excellent leveling.

The following examples illustrate the present invention. Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, all temperatures are in degrees Centigrade, and pressure is at or near atmospheric pressure.

25 COMPARATIVE EXAMPLE 1

An electroplating bath is prepared to contain 82.8 ml/L liquid nickel chloride, 434.8 ml/L liquid nickel sulfate, 18.7 g/L cobalt sulfate, 0.14 g/L dimethylamine borane, and 30.0 g/L boric acid. Liquid nickel chloride is an

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aqueous solution containing 720 g/L $\text{NiCl} \cdot 6\text{H}_2\text{O}$ or 180 g/L Ni metal, while liquid nickel sulfate is an aqueous solution containing 600 g/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ or 135 g/L Ni metal. The operating temperature is $50^\circ\text{C} \pm 2^\circ\text{C}$, and the pH is adjusted to 4.0 ± 0.2 with either H_2SO_4 or HCl .

- 5 A metal deposit is produced from the electroplating bath with no additives, using 2 amp DC current in a mechanically agitated 267 ml Hull cell to determine plate response over a wide plating current density. Plating time is 5 minutes. The type/appearance of the metal plate is shown in Figure 2. A mirror bright deposit is obtained over a narrow current density range and at a relatively high
- 10 current densities, over 80 ASF.

COMPARATIVE EXAMPLE 2

The electroplating bath of Comparative Example 1 is prepared except that 0.05 g/L of sodium laurel sulfate as a surfactant and 2.25 g/L of sodium saccharin as a stress reliever are added.

- 15 A metal deposit is produced from the electroplating bath with a surfactant and a stress reducing agent, using 2 amp DC current in a mechanically agitated 267 ml Hull cell to determine plate response over a wide plating current density. Plating time is 5 minutes. The type/appearance of the metal plate is shown in Figure 3. A mirror bright deposit is obtained over at current densities of about 40
- 20 ASF and higher.

COMPARATIVE EXAMPLE 3

The electroplating bath of Comparative Example 1 is prepared except that 0.1 g/L of sodium 2-ethylhexyl sulfate as a surfactant and 1 g/L of bisbenzenesulfonimide as a stress reliever are added.

- 25 A metal deposit is produced from the electroplating bath with a surfactant and a stress reducing agent, using 2 amp DC current in a mechanically agitated 267 ml Hull cell to determine plate response over a wide plating current density.

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Plating time is 5 minutes. The type/appearance of the metal plate is shown in Figure 3. A mirror bright deposit is obtained over at current densities of about 40 ASF and higher.

EXAMPLE 1

5 The electroplating bath of Comparative Example 1 is prepared except that 0.05 g/L of sodium laurel sulfate as a surfactant, 2.25 g/L of sodium saccharin as a stress reliever, 0.01 g/L of 2-butyne-1,4-diol and 0.01 g/L of propargyl alcohol as brighteners, and 0.10 g/L of 1-(sulfopropyl)pyridinium hydroxide as a leveler are added.

10 A metal deposit is produced from the electroplating bath with a surfactant, a stress reducing agent, and brighteners using 2 amp DC current in a mechanically agitated 267 ml Hull cell to determine plate response over a wide plating current density. The electroplating bath using a standard make up requires 6.2 Volts to achieve 2 amps. Plating time is 5 minutes. The
15 type/appearance of the metal plate is shown in Figure 4. A mirror bright deposit is obtained over at a wide range of current densities as low as about 4 ASF and higher.

EXAMPLE 2

20 The electroplating bath of Comparative Example 1 is prepared except that 0.1 g/L of sodium 2-ethylhexyl sulfate as a surfactant, 1 g/L of bisbenzenesulfonimide as a stress reliever, 0.01 g/L of 2-butyne-1,4-diol and 0.02 g/L of propargyl alcohol as brighteners, and 0.08 g/L of (1-sulfo-2-hydroxypropyl)pyridinium hydroxide as a leveler are added.

25 A metal deposit is produced from the electroplating bath with a surfactant, a stress reducing agent, and brighteners using 2 amp DC current in a mechanically agitated 267 ml Hull cell to determine plate response over a wide plating current density. Plating time is 5 minutes. The type/appearance of the

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metal plate is shown in Figure 4. A mirror bright deposit is obtained over at a wide range of current densities as low as about 4 ASF and higher.

EXAMPLE 3

5 The electroplating bath of Example 1 is prepared except that a 100 g/L of sodium sulfate decahydrate is added via the make up. Voltage is lowered to 5 Volts to achieve 2 amps without impacting the type/appearance of the metal plate.

EXAMPLE 4

10 The electroplating bath of Example 1 is prepared except that a 30 g/L of potassium chloride is added via the make up. Voltage is lowered to 4.3 Volts to achieve 2 amps without impacting the type/appearance of the metal plate.

While the invention has been explained in relation to certain embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification.
15 Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.